

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)



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Applicant's or agent's file reference TS1227 PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/51106	International filing date ( <i>day/month/year</i> ) 29.12.2003	Priority date ( <i>day/month/year</i> ) 30.12.2002
International Patent Classification (IPC) or both national classification and IPC C10G65/04		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ.. et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  21.07.2004	Date of completion of this report  15.04.2005
Name and mailing address of the International preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Deurinck, P  Telephone No. +31 70 340-2404  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/51106**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-20 as originally filed

**Claims, Numbers**

1-12 received on 21.12.2004 with letter of 21.12.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
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International application No. **PCT/EP 03/51106**

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	3-5,7,8,10,11
	No: Claims	1,2,6,9,12
Inventive step (IS)	Yes: Claims	
	No: Claims	1-12
Industrial applicability (IA)	Yes: Claims	1-12
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

## AD V:

### 1. Novelty (Art. 33(2) PCT)

#### 1.1

The present application does not meet the requirements of Article 33 PCT, because the subject-matter of independent **Claims 1, 2, 9 and 12** is not new.

Document D1 discloses a process for the preparation of aliphatic paraffins from a Fischer-Tropsch product comprising

- a Fischer-Tropsch process producing hydrocarbons
- fractionating the Fischer-Tropsch product to separate a cut boiling point upon to about 650°F (C<sub>4</sub>-C<sub>20</sub>) including any narrower boiling range fraction within such range (see D1: column 3, lines 58-67)
- hydrogenating the fraction to saturate the olefinic hydrocarbons (see D1: column 5, lines 48-57); and
- separating a fraction comprising detergent hydrocarbons via distillation (see D1: column 6, line 66 - column 7, line 59; claim 1).

The aliphatic paraffins can then be converted to normal olefins via dehydrogenation (see D1: column 1, lines 61-67). These straight chain alkyl groups constitute a preferred structure of the long chain alkyl substituents in detergents (see D1: column 1, lines 31-45).

#### 1.2

The present application does not meet the requirements of Article 33 PCT, because the subject-matter of **Claim 6** is not new.

Document D2 discloses an integrated process for preparing detergents, comprising

- a Fischer Tropsch process producing hydrocarbons (see D2: column 2, lines 58-65; column 16, lines 15-25);
- a separation process producing a C<sub>2-5</sub> stream, a C<sub>6-8</sub> stream (see D2: column 6, lines 10-21), a C<sub>18-26</sub> stream or C<sub>9-17</sub> stream (see D2: column 16, lines 15-25) and a C<sub>27+</sub> stream or C<sub>17+</sub> stream (see D2: column 8, lines 27-32);
- a hydrotreatment process to remove oxygenates from the C<sub>9-17</sub> stream (see D2:

column 6, lines 54-55);

- a dehydrogenation process to produce a detergent hydrocarbon stream comprising monoolefins (see D2: column 16, lines 14-34); and
- a conversion process to produce detergents (see D2: claim 1).

The C<sub>17+</sub> stream can be hydrocracked to produce a fuel (see D2: column 8, lines 27-33).

## 2. Inventive steps (Art. 33(3) PCT)

### 2.1

The present application does not meet the requirements of Article 33 PCT, because the subject-matter of independent **Claim 8** does not involve an inventive step in the sense of Article 33(3) PCT.

*Document D1* is considered to represent the most relevant state of the art.

The subject-matter of Claim 8 differs from D1 in the heavy fraction of the Fischer-Tropsch product is hydrocracked/hydroisomerised to prepare a hydrocarbon fuel whereas in D1 nothing is mentioned about hydrocracking/hydroisomerising the heavy fraction (*distinguishing feature*).

*The technical effect* that is achieved with this distinguishing feature is to produce a hydrocarbon oil.

*The problem to be solved* by the present invention may be regarded as: "To provide an improved process in order to produce a hydrocarbon fuel".

*Document D2* discloses an integrated process for preparing detergents (see D2: column 2, lines 58-65; column 6, lines 10-55; column 8, lines 27-32; column 16, lines 15-34; claim 1).

Starting from the disclosure of D1 and intending to solve the above-mentioned problem, a person skilled in the art had an incentive from D2 to produce a fuel from the heavy Fischer-Tropsch fraction.

Thus the subject-matter of independent Claim 8 does not involve an inventive step.

## 2.2

Document D3 discloses a process for producing detergents comprising

- a Fischer-Tropsch process producing hydrocarbons;
- fractionating the Fischer-Tropsch product to separate a C<sub>9</sub>-C<sub>15</sub> fraction (see D3: page 3, lines 53-58);
- separating a fraction comprising detergent hydrocarbons via distillation (see D3: Example 1).
- a dehydrogenation process to produce a detergent hydrocarbon stream comprising monoolefins (see D3: page 5, lines 30-37); and
- a conversion process to produce detergents (see D3: page 6, lines 52-57; claim 1).

The following dependent Claims are also not inventive:

- **Claim 4:** see D2: column 6, lines 9-15;
- **Claim 5:** see D2: figure 1; claim 1;
- **Claim 7:** see D3: claim 1; see D2: claim 1;
- **Claim 11:** see D2: column 8, lines 27-33;

## 2.3

There is no evidence on file that the additional technical features of dependent **Claims 3 and 10** might cause a technical effect. Consequently, it cannot be seen which technical problem is solved. Therefore, an inventive step cannot be acknowledged.

TS 1227C L A I M S

1. A process for the preparation of detergents, comprising separating the hydrocarbonaceous product stream from a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C<sub>18</sub>-hydrocarbons, preferably the light fraction comprising at least 90 %wt, more preferably at least 95 %wt, of C<sub>18</sub>-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenation of at least part of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons, dehydrogenation of at least part of the detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins and conversion of the mono-olefins into detergents.

2. A process for the preparation of detergents in which process a hydrogenated product, which product is obtained by separating the hydrocarbonaceous product stream from a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C<sub>18</sub>-hydrocarbons, preferably the light fraction comprising at least 90 %wt, more preferably at least 95 %wt, of C<sub>18</sub>-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenation of at least part of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into

saturated hydrocarbons and distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons, is dehydrogenated to obtain a detergent hydrocarbon stream comprising mono-olefins, followed by conversion of the mono-olefins into detergents.

3. A process according to claim 1 or 2, in which the light fraction comprises mainly, preferably 90 %wt, more preferably 95 %wt, C<sub>16</sub>-hydrocarbons, more especially mainly, preferably 90 %wt, more preferably 95 %wt, C<sub>14</sub>-hydrocarbons.

4. A process according to any of claims 1 to 3, in which the hydrocarbonaceous product stream of the Fischer-Tropsch process, before separation into the light fraction and the heavy fraction, is separated into a light stream, comprising most, suitably at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, of the C<sub>1</sub>-C<sub>4</sub> hydrocarbons produced in the Fischer-Tropsch process, especially the light product stream comprising most, suitably at least 80 %wt, preferably 90 %wt, more preferably 95 %wt, of the C<sub>1</sub>-C<sub>3</sub> hydrocarbons produced in the Fischer-Tropsch process, and optionally unconverted synthesis gas constituents, carbon dioxide and other inert gasses, and a heavy stream which is separated into the light and the heavy fraction.

5. A process according to any of claims 1 to 4, in which process also a light product is removed from the hydrocarbonaceous product stream from the Fischer-Tropsch process or the light stream, the light product stream containing mainly the C<sub>7</sub>-products, preferably the C<sub>8</sub>-products, more preferably the C<sub>9</sub>-products, present in the stream, especially the light product comprising at least 90 %wt, more preferably at least 95 %wt, of the



C<sub>7</sub>-products present, more especially the light product comprising at least 90 %wt, preferably at least 95 %wt, of the C<sub>8</sub>-products present, still more especially the light product comprising at least 90 %wt, more preferably at least 95 %wt, of the C<sub>9</sub>-products present.

6. A process according to any of claims 1 to 5, in which the light fraction which is to be hydrogenated comprises mainly C<sub>9</sub>- to C<sub>18</sub>-hydrocarbons, preferably at least 80 %wt C<sub>9</sub>- to C<sub>18</sub>-hydrocarbons, more preferably at least 90 %wt, especially the light fraction comprises mainly C<sub>10</sub>- to C<sub>13</sub>-hydrocarbons, preferably at least 80 %wt C<sub>10</sub>- to C<sub>13</sub>-hydrocarbons, more preferably at least 90 %wt, or the light fraction comprises mainly C<sub>14</sub>- to C<sub>17</sub>-hydrocarbons, preferably at least 80 %wt C<sub>14</sub>- to C<sub>17</sub>-hydrocarbons, more preferably at least 90 %wt, the distillation of the hydrogenated hydrocarbons being an optional feature.

7. A process according to any of claims 1 to 6, in which the conversion of the mono-olefins into detergents comprises at least one step selected from:

- alkylation with benzene or toluene optionally followed by sulfonation and neutralisation;
- alkylation with phenol followed by at least one of alkoxylation, sulfonation and neutralisation, sulfation and neutralisation or alkoxylation combined with oxidation;
- hydroformylation optionally followed by at least one of alkoxylation, glycosylation, sulfation, phosphatation or combinations thereof
- sulfonation;

- epoxidation;
- hydrobromination followed by amination and oxidation to amine oxide; and
- phosphonation.

8. A process for the preparation of detergents and hydrocarbon fuels from the product stream of a Fischer-Tropsch process, comprising a process as described in any of claims 1 to 7 for the preparation of detergents from a light fraction of the Fischer-Tropsch process in combination with the hydrocracking/hydroisomerisation of the one or more heavy fractions of the Fischer-Tropsch process.

9. A process for the preparation of detergent hydrocarbons comprising separating the hydrocarbonaceous product stream of a Fischer-Tropsch process producing normally liquid and normally solid hydrocarbons into a light fraction comprising mainly C<sub>18</sub>-hydrocarbons, preferably C<sub>16</sub>-, more preferably C<sub>14</sub>-hydrocarbons, and one or more heavy fractions comprising the remaining hydrocarbons, hydrogenation of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons and optionally dehydrogenation of at least part of the detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins.

10. A process according to claim 9, in which any one or more reject streams in the process for the preparation of detergent hydrocarbons are used as additional feedstreams in the process for the preparation of fuels.

11. A process for the preparation of detergent hydrocarbons and hydrocarbon fuels from the product

stream of a Fischer-Tropsch process, comprising a process as described in claim 9 or 10 for the preparation of detergent hydrocarbons from a light fraction of the Fischer-Tropsch process in combination with the hydrocracking/hydroisomerisation of the heavy product stream of the Fischer-Tropsch process.

12. A process for the preparation of detergents comprising dehydrogenation of detergent hydrocarbons to obtain a detergent hydrocarbon stream comprising mono-olefins and conversion of the mono-olefins into detergents, the detergent hydrocarbons being prepared by separating the product stream of a Fischer-Tropsch process into a light fraction comprising mainly C<sub>18</sub>-hydrocarbons, preferably C<sub>16</sub>-, more preferably C<sub>14</sub>-hydrocarbons, and a heavy fraction comprising the remaining hydrocarbons, hydrogenation of the light fraction to convert unsaturated hydrocarbons and/or oxygenates into saturated hydrocarbons, distillation of product thus obtained into at least one fraction comprising detergent hydrocarbons.